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**Combined electrochemical treatment / biological process for the removal of a  
commercial herbicide solution, U46D®**

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**Abstract**

The removal of a commercial solution of 2,4-D, U46D<sup>®</sup>, was carried out by coupling an electrochemical oxidation and a biological process involving activated sludge.

The similar electrochemical behavior of 2,4-D and U46D<sup>®</sup> highlighted their oxidation around 1.6 V/SCE and the feasibility of an electrochemical pretreatment. It was based on a home-made flow cell involving bare graphite felt electrode. To propose a consistent mechanism for 2,4-D oxidation, the indirect determination of •OH has been performed and the absence of radicals formation during 2,4-D electrolysis was confirmed. Consequently, the proposed pretreatment can be considered as a 'direct' electrochemical process instead of an advanced electrochemical oxidation process.

The impact of the flow rate on the pretreatment showed that 3 mL min<sup>-1</sup> was a good compromise between the pretreatment time and the electrolysis efficiency, since it led to an almost total degradation of the pollutant while its mineralization remained limited. At this flow rate and for 500 mg L<sup>-1</sup> of 2,4-D, the energy cost was estimated at 5 kWh m<sup>-3</sup>. The biodegradability of U46D<sup>®</sup> solution was not significantly modified after electrolysis, most likely due to the presence of dimethylamine salt in U46D<sup>®</sup>. Owing to the significant BOD<sub>5</sub>/COD ratio measured, a biological treatment of the commercial U46D<sup>®</sup> solution was however considered.

The electrochemical pretreatment shortened the duration of the biodegradation. For non-pretreated U46D<sup>®</sup> (100 mg L<sup>-1</sup> 2,4-D), mineralization remained limited until 6 days of culture (33.7% DOC removal), and total removal of the DOC was observed after 8 days. For pretreated U46D<sup>®</sup>, 63.7% decrease until the fifth day of culture was observed but total mineralization was not reached at the end of culture (72.1%). An overall mineralization yield during the coupled process of 82.1% was therefore reached. The presence of refractory

compounds generated during the electrochemical pretreatment in small concentration was therefore shown.

**Key-words.** Commercial pesticide U46D<sup>®</sup>; Combined process; Electrochemical process; Biological treatment; Activated sludge.

## 1. Introduction

Electrochemical processes for pesticides removal have been mainly investigated from the nineties. The adaptability and applicability to different volumes, media and pollutants as well as the possibility and ease of automation (current intensity or electrode potential are easy to control) constitute obvious advantages of electrochemical processes [1-3]. Moreover, these processes can be applied to flow systems [4].

Concerning pesticides removal, three main processes are studied: electro-coagulation, electro-oxidation and electro-Fenton.

Electro-coagulation is based on the soluble anodes principle. When current intensity or potential is generated between two electrodes (in general iron or aluminum electrodes), the corresponding ions are produced which entails the generation of coagulants in solution and then the coagulation-flocculation of pollutants [5]. For example, when a sacrificial iron anode is implemented, the produced ferrous ions are oxidized to ferric ions which precipitate into  $\text{Fe}(\text{OH})_3$ . The metallic hydroxide is produced in order to reach a sufficient concentration to initiate polymerization or condensation reactions [6, 7]. Fine hydrogen and oxygen bubbles produced at the cathode and anode surfaces, respectively drag particles in suspension to solution surface by electroflotation. This process is effective in mild conditions (of temperature and turbidity) unlike in chemical coagulation. However, electro-coagulation being a non-degradative process, produced flocs should be removed by decantation, flotation

or filtration. Moreover, the anodes have to be regularly replaced and electrodes passivation may occur limiting the process efficiency [8]. An enhanced electro-coagulation method (peroxy-coagulation) was reported by Brillas et al. [9]. This method is partially degradative and thus reduces the volume of produced sludge. Coagulation occurs simultaneously with Fenton's reaction between  $\text{Fe}^{2+}$  ions and cathodically produced  $\text{H}_2\text{O}_2$ .

The anodic oxidation or electro-oxidation is an Electrochemical Advanced Oxidation Process (EAOP) based on the production of a strong oxidant, the hydroxyl radical  $\text{M}(\cdot\text{OH})$ . The mineralization efficiency depends on three crucial factors: the hydroxyl radical generation, the nature and the stability of the electrode material and the competition of oxygen release. Adsorbed hydroxyl radicals are generated at the anode surface via water oxidation, and interactions between hydroxyl radicals and the anode surface depend on the electrode material. The electrode is considered as “active” when this interaction is strong and characterized by a low oxygen overpotential; it is the case for  $\text{IrO}_2$  based electrodes [10]. In this case, oxygen release is favored at the expense of reactions between adsorbed hydroxyl radicals and organic compounds [11] and then mineralization yields are reduced. In the case of strong oxygen overpotential, the oxidation of organic compounds by hydroxyl radicals is favored near the electrode surface, and consequently, the electrode is considered as “non-active”. BDD is one of the best material for this type of electrode due to its large  $\text{O}_2$  evolution overpotential and high electrochemical stability [12] and was thus largely studied [13-16]. Pt,  $\text{PbO}_2$ ,  $\text{SnO}_2$  electrodes have been also extensively investigated [17-19]. For all these studies, mineralization yields exceeded 75% and reached up to 100% for current densities from 75 to 150  $\text{mA cm}^{-2}$ .

Other electrode materials have also been used for pesticide removal, such as Dimensionally Stable Electrode (DSA), which are constituted of a titanium support covered by a conductive film of metallic oxide or metallic oxides alloys. According to the nature of the conductive

film, they can be “active” or “non-active” [20, 21]. In order to increase the mineralization yields, sodium chloride can be added to the electrolyte solution for the production of new oxidant such as  $\text{Cl}_2$  or  $\text{ClO}_2$ ; this indirect oxidation can be carried out as an alternative to the direct production of hydroxyl radicals [4, 22].

In the electro-Fenton process, hydrogen peroxide is generated *in situ* by the two electrons reduction of oxygen at the cathode surface, as well as the regeneration of ferrous ions. Compared to a classical Fenton process, the *in situ* production of reactants prevents from their consumption in large amounts and the regeneration of the catalyst avoids its accumulation as ferric ions, thus decreasing the formation of sludge. At optimized conditions there is no sludge formation since  $\text{Fe}^{3+}$  does not precipitate at pH 3 for a concentration lower than 0.1 mM, which is used in carbon felt version. Graphite felt cathodes [23-25] and oxygen gas diffusion electrodes [26-29] are the most commonly used electrodes. Various types of Fenton-like processes can be performed [30]; ferrous ions can be directly added to the solution or produced from the oxidation of a sacrificial iron anode (Fered-Fenton). Hydrogen peroxide can also be added to the solution or generated at the cathode surface.

Pesticide removal has been largely studied by the electro-Fenton process [31] and mineralization yields are similar to those obtained by electro-oxidation [23]. Electro-Fenton process allows some adaptations especially concerning electrode materials and cell design. For example, a BDD anode can be added in the electrochemical cell to improve the mineralization rate thanks to a concomitant production of hydroxyl radicals [26]. A very good example of the electro-Fenton process using a BDD anode was carried out by Oturan et al. [32] when they studied the mineralization of atrazine and cyanuric acid. More recently, the photoelectro-Fenton process was envisaged to increase the performances of electro-Fenton [28, 29, 33].

Electro-oxidation and electro-Fenton are efficient processes leading to high mineralization yields. In order to mineralize organic recalcitrant compounds, an alternative is the coupling of a physico-chemical treatment with a biological process. It can be interesting from an economical point of view since for this type of effluent, the use of an AOP is estimated at 10-20 € m<sup>-3</sup> at industrial scale, while the coupling of solar photo-Fenton treatment and biological process was recently estimated at 7 € m<sup>-3</sup> [34].

Several electrochemical processes have been carried out after a biological treatment. For example, Ti/RuO<sub>2</sub>-IrO<sub>2</sub> electrodes [35] or BDD [36] have been used for the disinfection of biological pretreated domestic effluent, and Ti/BDD was employed during a coke waste water post-treatment [37].

An electrochemical process can also be performed as a pre-treatment in order to increase effluent biodegradability and/or reduce its toxicity. To achieve the complete mineralization of the effluent at the end of the combined process, the decrease of DOC should remain limited during this electrochemical pretreatment step. Indeed, significant residual organic carbon should remain available as a carbon substrate for microorganisms during the subsequent biological process [38, 39]. In order to increase industrial effluents biodegradability, various electrode materials have been studied such as platinum [40], stainless steel [41], Ti/RuO<sub>2</sub>-IrO<sub>2</sub> [42-44] or Pb/PbO<sub>2</sub> [45]. Similarly, electro-oxidation and electro-Fenton have been studied as pretreatments prior to a biological process [42, 44-47].

With an integrated system, the risk is to decrease the efficiency of the biological treatment [48], because the production of strong oxidant such as hydroxyl radical can inhibit microorganisms metabolism. In order to prevent this inhibition, both processes can be separated, for instance in the case of Acetomipride (1000 mg L<sup>-1</sup>) removal; it was first oxidized with a BDD anode and then biologically treated by means of an activated sludge biofilter, with the solution circulating from one to the other [48].

In order to improve biodegradability in view of a subsequent biological treatment, namely when total mineralization of the effluent is not needed, direct oxidation or reduction of recalcitrant compounds on an active electrode such as graphite felt can also be considered, even though the corresponding literature remains scarce [49-52]. The aim is to better target the electrochemical reaction, which would be useful not only from an economical point of view, but also in order to control the formation of by-products. A more selective pre-treatment could thus prevent from the formation of more toxic compounds, as it has already been shown in some AOPs and EAOPs processes [51]. Such a direct electrode reaction led to promising results for 2,4-D, a chlorinated phenoxy acid herbicide [51, 52]. Indeed, we have previously shown that mild oxidation of the target compound can be sufficient to improve the biodegradability of 2,4-D solutions [51] allowing a subsequent biological treatment [52]. To complete this previous work and to approach real conditions, the removal of a commercial solution of 2,4-D named U46D<sup>®</sup> has been tested by mild oxidation coupled with activated sludge treatment.

## 2. Materials and Methods

### 2.1. Chemicals

2,4-dichlorophenoxyacetic acid (2,4-D) (98%) was purchased from Alfa Aesar (Schiltigheim, France) and U46D<sup>®</sup> was commercialized by SAS Nufarm (Gennevilliers, France). Chlorohydroquinone (85%) was purchased from Sigma-Aldrich (Saint-Quentin Fallavier, France). Acetonitrile (ACN) and formic acid were LC/MS grade from JT Baker (Deventer, Netherlands). All standards were prepared with ultra pure water (PurelabOptions-Q7/15, Elga, 18.2 M $\Omega$  cm).



## 2.2. Electrochemical pre-treatment

The electrochemical pre-treatment was based on a home-made flow cell [51]. Graphite felt used as working electrode was supplied by Le Carbone Lorraine (RVG 4000 – Mersen, Paris La Défense, France). Its specific area, measured by the BET method, was  $0.7 \text{ m}^2 \text{ g}^{-1}$ ; its density was  $0.088 \text{ g cm}^{-3}$  and its carbon yield was 99.9%.

Two interconnected stainless steel plates were used as counter-electrodes and compartments were separated by cationic exchange membranes (Ionac 3470 – Lanxess SAS, Courbevoie, France). The reference electrode (Saturated Calomel Electrode – SCE) was positioned in the middle of the graphite felt, and the potential control was performed using a VersaSTAT 3 potentiostat from Ametek/Princeton Applied (Elancourt, France). To ensure a good homogeneity of the potential distribution in the three dimensional working electrode, the felt was located between the two counter-electrodes [53]. The cell was thoroughly rinsed with distilled water before and after each experiment. The electrolyte solution percolated the porous electrode and flow rate was monitored by a Gilson minipuls 2 peristaltic pump (Middleton, WI, USA).

## 2.3. Biological process

Activated Sludge used in this study was collected from a local wastewater treatment plant in Rennes (Rennes Beaurade, France). It was washed several times by a succession of centrifugations. After each washing, activated sludge was centrifuged at 3000 rpm for five minutes (Jouan, Thermo Fisher Scientifics, Saint Herblain, France). The supernatant was then separated from the sludge to remove any residual carbon or mineral source.

Culture medium was prepared in triplicate in 500 mL Erlenmeyer flasks containing 250 mL of either pre-treated solutions or pure U46D<sup>®</sup> solutions. Minerals were spiked in the medium as highly concentrated solutions to reach the following initial composition (mg L<sup>-1</sup>): Na<sub>2</sub>HPO<sub>4</sub>, 334; K<sub>2</sub>HPO<sub>4</sub>, 208; KH<sub>2</sub>PO<sub>4</sub>, 85; CaCl<sub>2</sub>, 27.4; MgSO<sub>4</sub>·7H<sub>2</sub>O, 22.6; NH<sub>4</sub>Cl, 75; FeCl<sub>3</sub>·6H<sub>2</sub>O, 0.26; and the initial pH was adjusted to 7.0 ± 0.2. Activated sludge was added in order to achieve an initial concentration of 0.5 g L<sup>-1</sup> of dry matter. Cultures were agitated at 250 rpm, and kept at 30°C in aerobic conditions. Samples (5 mL) were taken regularly and filtered through 0.45 µm-syringe filters for measurements.

### 2.3. Analysis

Measurements of the residual 2,4-D and chlorohydroquinone concentration were performed by HPLC (High Performance Liquid Chromatography) (Milford, USA) system involving a pump Waters 600, fitted with a Phenomenex Kinetex<sup>®</sup> C18 2.6 µm column (4.6 mm × 100 mm), along with a Waters 996 Photodiode array detector, a Waters 717 pH Autosampler and controlled through an Empower<sup>®</sup> 2 program. The mobile phase consisted of acetonitrile and trifluoroacetic acid (TFA) 0.1% in ultra-pure water with a ratio of 30/70 at 1 mL min<sup>-1</sup>.

GC/MS/MS measurements were performed with a Perkin Elmer Clarus 500 apparatus coupled with a Variance CB-FFAP 0.25 µm column (25 m × 0.15 mm). Compounds identification was performed with the help of a List database.

#### 2.3.1. Dissolved Organic Carbon (DOC) measurements

Solutions were filtered on Satorius Stedim Minisart 0.45 µm GF prefilters (Goettingen, Germany). DOC was measured by means of a TOC-V<sub>CPH/CPN</sub> Total Organic

Analyzer Shimadzu. Organic carbon compounds were combusted and converted to CO<sub>2</sub>, which was detected and measured by a non-dispersive infrared detector (NDIR). Reproducible DOC values were always obtained using the standard NPOC (Non Purgeable Organic Carbon) method.

### 2.3.2. Chemical Oxygen Demand (COD) and Biological Oxygen Demand after 5 days (BOD<sub>5</sub>)

Chemical Oxygen Demand (COD) was measured by means of a Test Nanocolor® CSB 160 from Macherey-Nagel (Düren, Germany). The amount of oxygen required for the oxidation of the organic and mineral matter at 164°C for 30 min was quantified after oxidation with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> at acidic pH and heating.

BOD<sub>5</sub> measurements were carried out in Oxitop IS6 (WTW, Alès, France). Activated sludge provided by a local wastewater treatment plant (Rennes Beaurade, Bretagne, France) was used to inoculate duplicate flasks and the initial microbial concentration was 0.5 g L<sup>-1</sup>. Control flasks containing easily biodegradable compounds (glucose and glutamic acid at 150 mg L<sup>-1</sup> each) were run at the same time; and blank flasks, for which the sample was replaced by water, were used to deduce the biological oxygen demand corresponding to the endogenous respiration.

Activated sludge solution volume to be added in each flask was deduced from the range of expected BOD<sub>5</sub> values, given by  $BOD_5 = COD/1.46$ .

The following mineral basis was used for all experiments (g L<sup>-1</sup>): MgSO<sub>4</sub>·7H<sub>2</sub>O, 22.5; CaCl<sub>2</sub>, 27.5; FeCl<sub>3</sub>, 0.15; NH<sub>4</sub>Cl, 2.0; Na<sub>2</sub>HPO<sub>4</sub>, 6.80; KH<sub>2</sub>PO<sub>4</sub>, 2.80. Before use, KOH was added to achieve neutral pH (7.0 ± 0.2) and nitrification inhibitor (10 mg L<sup>-1</sup> solution of *N*-Allylthiourea) was added.

### 3. Results and Discussion

#### 3.1. Electrochemical pretreatment

GC/MS analysis showed that the commercial herbicide U46D<sup>®</sup> was mainly composed of 2,4-D and dimethylamine salt (data not shown). Other compounds were detected at trace levels, such as 2,4-dichlorophenol or xylene (dimethyl benzene).

Previous study [51] highlighted that 2,4-D can be oxidized at 1.6 V/SCE on graphite felt electrode. Figure 1 represents the voltammogram obtained with a solution of U46D<sup>®</sup> (500 mg L<sup>-1</sup>) in Na<sub>2</sub>SO<sub>4</sub> 0.1 M, showing similar electrochemical behavior in oxidation to that observed for pure 2,4-D.

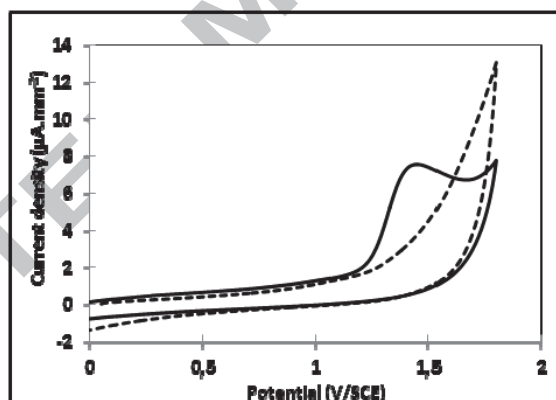


Fig.1. Cyclic Voltammetry of U46D<sup>®</sup> (500 mg L<sup>-1</sup>, continuous line) in 0.1 M Na<sub>2</sub>SO<sub>4</sub> (dotted line), 100 mV s<sup>-1</sup>, glassy carbon electrode (7 mm<sup>2</sup>).

An electrochemical pretreatment of the commercial 2,4-D solution was therefore performed and was first investigated at 1.6 V/SCE with 1 mL min<sup>-1</sup> flow rate. Electrolysis was then carried out at a constant current intensity of 200 mA, which corresponds to the current intensity measured during the electrolyses at 1.6 V/SCE. Working at a constant

current intensity would be helpful for an industrial purpose, since at large scale the reference electrode cannot be used. After electrolysis, high elimination yield, 95.5%, was obtained in only one pass through the flow-cell, similar to those obtained for pure 2,4-D solutions [51]. This result confirmed the feasibility of the electrochemical pre-treatment and was promising for the electrolysis of high amounts of pesticides since the recycling of the solution was not needed.

### 3.2. Nature of the electrochemical process

The production of hydroxyl radicals is closely linked to the electrode material used and then to oxygen overvoltage. Mechanisms involving  $\bullet\text{OH}$  have been previously proposed in studies based on electrochemical oxidation on graphite felt [54]. If some electrodes (boron doped diamond for instance) are well-known to be powerful candidates for  $\bullet\text{OH}$  generation, from a thermodynamic point of view, the formation of hydroxyl radicals on graphite felt seems unlikely for potentials lower than 2 V/SCE. Indeed, with a standard potential of 2.80 V/SHE for  $\bullet\text{OH}/\text{H}_2\text{O}$ , the oxidation potential at pH 7 reaches 2.38 V/SHE (decrease of 0.06 V per unit of pH) *i.e.* 2.13 V/SCE. Therefore, in order to conclude on the electrochemical oxidation phenomena occurring during the use of such material and to confirm the specificity and selectivity of the considered process, namely a direct oxidation at the electrode surface, the indirect determination of the hydroxyl radicals has been realized.

$\bullet\text{OH}$  are known for their strong reactivity with benzene (kinetic rate constant  $k = 8 \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ), showing the relevance of this compound as a radicals' scavenger [55, 56]. Since phenol is the sole product of benzene hydroxylation, it is possible to deduce the amount of  $\bullet\text{OH}$  produced from the monitoring of benzene degradation ( $\lambda=200 \text{ nm}$ ) linked to phenol production ( $\lambda=270 \text{ nm}$ ).

From this, and after checking the absence of direct benzene oxidation at the electrode at 1.6 V/SCE, electrolysis was performed (20 mM initial benzene concentration) in the flow-cell with recycling of the electrolyzed solution. Neither noticeable benzene degradation nor phenol formation could be observed after 140 min of electrolysis. This result clearly confirmed that in the considered experimental conditions and electrolysis time, oxidation of water on graphite felt did not result in  $\bullet\text{OH}$  formation. Furthermore and contrarily to electrolysis of the 2,4-D or U46D<sup>®</sup> solutions, the recycling of the electrolysis solution through the cell was considered for this experiment, which was in favor of phenol formation from benzene hydroxylation, confirming unambiguously the absence of radicals formation during 2,4-D electrolysis. Consequently, the proposed pretreatment can be considered as a ‘direct’ electrochemical process instead of an advanced electrochemical oxidation process.

### 3.3. Impact of the flow rate on pretreatment efficiency

A flow rate of 1 mL min<sup>-1</sup> was previously considered owing to the high degradation yields obtained if compared to those observed at higher flow rates [49, 50]. The percolation flow rate necessarily impacts the time-contact of the effluent with the polarized surface of the graphite felt. The impact of the percolated flow rate on pretreatment efficiency was therefore investigated, at a constant potential and then at a constant current intensity.

#### 3.3.1. Chronoamperometry study

##### 2,4-D degradation

As seen above, electrolysis of 2,4-D performed at 1.6 V/SCE with 1 mL min<sup>-1</sup> flow rate led to 96% degradation with only a single pass through the cell [51]. To check the influence of the flow rate on the degradation yield, it was examined in the range 1 to 10 mL min<sup>-1</sup> (Table 1).

Flow rate (mL min <sup>-1</sup> )	1	2	3	5	10
<b>2,4-D Degradation yield (%)</b>	>99.9	>99.9	99.3	83.3	46.6
<b>Oxidation yield (%)</b>	54.1	35.6	32.2	24.7	10.3
<b>Mineralization yield (%)</b>	54.2	38.7	35.2	27.2	14.7

**Table 1:** Influence of the flow rate on degradation (2,4-D decrease), oxidation (COD removal) and mineralization (TOC removal) yields during chronoamperometry study.

Until 3 mL min<sup>-1</sup>, more than 99% degradation of the 2,4-D present in the commercial herbicide U46D<sup>®</sup> was observed, and decreased to 83% for 5 mL min<sup>-1</sup> and until only 46% for 10 mL min<sup>-1</sup>.

The decrease in the yield is related to insufficient residence time in the graphite felt with less contact of electro-active species with the electrode surface. Indeed, since the reaction involves a rapid electron transfer between the substrate and the electrode, an increase of the flow rate probably leads to the apparition of preferential flow paths through the felt, owing to its high porosity. Therefore, the decrease of the degradation yield with the flow rate is most likely linked to the low contact between the solution and the electrode fibers, rather than slow reaction kinetics.

A flow rate of 3 mL min<sup>-1</sup> appeared therefore to be a good compromise between the time of electrolysis, linked to the energy cost, and the efficiency. However, and to confirm the relevance of this flow rate, other parameters should be examined, such as mineralization, oxidation, by-products toxicity and biodegradability improvement.

#### *Mineralization and oxidation*

Impact of the flow rate of percolation on mineralization and oxidation at 1.6 V/SCE is displayed in table 1, showing that DOC and COD removal followed similar trends (table 1).

Mineralization decreased significantly when the flow rates increased from 1 to 2 mL min<sup>-1</sup> (from 54.2 to 38.7%) and then the decrease was less pronounced; the same trend was observed for oxidation (from 54.1 to 35.6 %). These trends differed from that observed for 2,4-D, for which total degradation was observed until 3 mL min<sup>-1</sup> (table 1), thus showing the impact of the flow rate on the formed by-products. From this, a flow rate of 3 mL min<sup>-1</sup> still appeared to be a good compromise between the pretreatment time and electrolysis efficiency, since it led to an almost total pollutant degradation while mineralization remained limited, both results being in favor of a subsequent biological treatment.

### 3.3.2. Chronopotentiometry study

Although the electrolyses performed at a constant potential were helpful regarding specificity (choice of a relevant potential related to the targeted compounds), it can present some drawbacks regarding possible subsequent industrial application. Indeed, it requires the use of a reference electrode, which is fragile and whose potential can vary with time (salt saturation, porous glass tip fouling...); in addition, with high surface 3-D electrodes, the potential homogeneity can appear difficult to control within all the electrode volume. Chronopotentiometry is therefore needed in view of a possible subsequent industrial implementation, since it does not require a reference electrode, but the problem of the homogenous potential distribution within the electrode volume remains. Indeed, when one counter-electrode is used, the potential field lines decrease rapidly within the felt and hence the reaction occurs only at the electrode surface in front of the counter-electrode. In the flow cell, the two counter-electrodes are positioned each side of the porous electrode, allowing a better linearization of the potential distribution [53]. To work in similar conditions as in the previously described chronoamperometry experiments, the electrode potential was measured



and the current intensity adjusted to obtain a potential close to 1.6 V/SCE, leading to applied current values of 200-250 mA.

Several electrolyses were performed at various flow rates (Fig. 2). As observed, and similarly to the behavior recorded in potentiostatic mode, high 2,4-D degradation yields were obtained until 3 mL min<sup>-1</sup> (above 95%), while they decreased above this flow rate (68 and 28% at 5 and 10 mL min<sup>-1</sup>, respectively) (Fig. 2a).

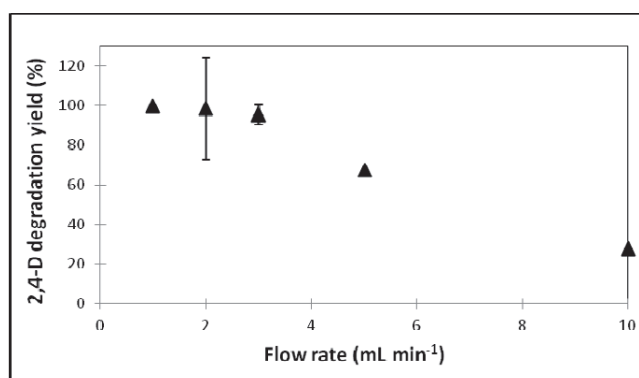


Fig. 2a. Influence of the flow rate on 2,4-D degradation yield during electrolysis performed at 200-250 mA with a single pass through the cell.

As observed in potentiostatic mode, DOC and COD removal followed similar trends: significant decrease of the levels of mineralization and oxidation were observed for 5 and 10 mL min<sup>-1</sup> (Figs. 2b and c). Therefore, chronopotentiometry can be applied as an electrochemical pretreatment of 2,4-D; and confirming the above results obtained in potentiostatic mode, 3 mL min<sup>-1</sup> appeared again to be a good compromise.

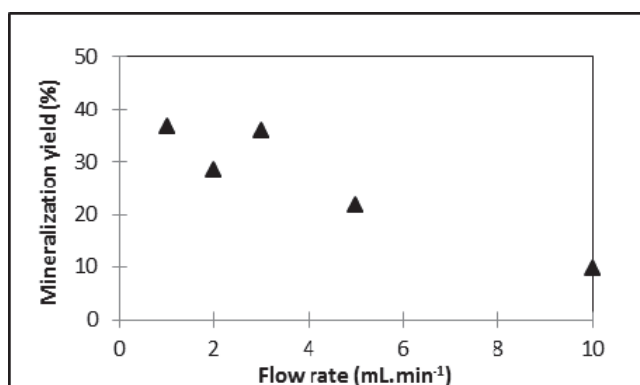


Fig. 2b. Influence of the flow rate on DOC removal during electrolysis performed at 200-250 mA with a single pass through the cell.

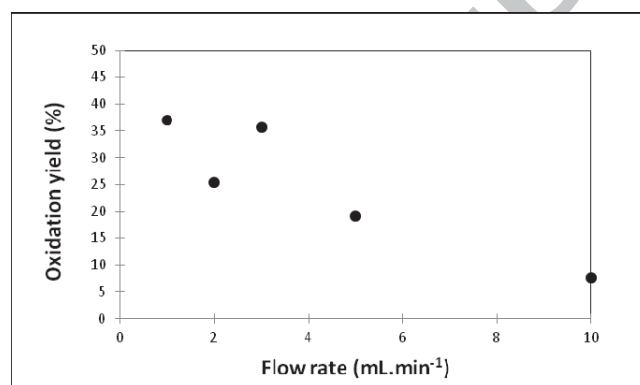


Fig. 2c. Influence of the flow rate on COD removal during electrolysis performed at 200-250 mA with a single pass through the cell.

### 3.4. Energy cost

For advanced electrochemical oxidation process, the estimation of energy costs is usually based on the COD removal (more especially for 80-85% COD removal) [57]. For example, for an electro-oxidation process carried out with a BDD anode, energy cost varied from 91 to 347 kWh m<sup>-3</sup> depending on the nature of the treated effluent, since initial COD was in the range 0.1 to 2 g L<sup>-1</sup> [58]. For the same electrode material and an initial COD of 1.75 g L<sup>-1</sup>, the energy cost has been estimated to 35 kWh m<sup>-3</sup> [59]. With a Pb/PbO<sub>2</sub> anode,

Panizza et al. [60] have estimated the operating costs at  $90 \text{ kWh m}^{-3}$  while they increased to  $681 \text{ kWh m}^{-3}$  with a three dimensional carbon bed electrode [61].

In this work, the energy cost cannot be estimated from COD removal, since after one pass through the electrolytic cell, COD removal never reached 80% and was more around 30-40%. Considering total 2,4-D degradation after one pass through the graphite felt electrode (2,4-D  $500 \text{ mg L}^{-1}$ , flow rate of  $3 \text{ mL min}^{-1}$  and applied current 220 mA), operating costs can be estimated to  $5 \text{ kWh m}^{-3}$  for the electrochemical pretreatment.

### 3.5. Biological treatment

#### 3.5.1. Biodegradability assessment

Biodegradability of solutions of U46D<sup>®</sup> electrolyzed at 200 mA and  $3 \text{ mL min}^{-1}$  flow rate was examined. Contrarily to pure 2,4-D for which the  $\text{BOD}_5/\text{COD}$  ratio increased from 0.04 to 0.25 [51], electrolysis did not improve the biodegradability of the commercial herbicide solution (Table 2). The initial  $\text{BOD}_5/\text{COD}$  ratio of U46D<sup>®</sup> may be related to the presence of dimethylamine salt, which is obviously more biodegradable than the target compound, 2,4-D, and hence improves the biodegradability of the commercial solution, if compared to pure 2,4-D. The final value nearly similar to that obtained after pure 2,4-D electrolysis may be related to the presence of similar by-products to those obtained after pure 2,4-D electrolysis [51].

Even though the  $\text{BOD}_5/\text{COD}$  ratio of 0.4 according to which an effluent can be considered as “easily biodegradable” [62, 63] was not reached, a biological treatment of the commercial U46D<sup>®</sup> solution may be considered owing to the significant ratio measured. Prior to activated sludge cultures, pretreatment in intermittent mode at  $1$  and  $3 \text{ mL min}^{-1}$  flow rate was therefore considered thereafter.

Solution	BOD <sub>5</sub> /COD
Pure 2,4-D	0.04 [49]
Pure electrolyzed 2,4-D	0.25 [49]
Non-electrolyzed U46D <sup>®</sup> solution	0.21
Electrolyzed U46D <sup>®</sup> solution	0.21

**Table 2:** Assessment of the biodegradability of pure and electrolyzed 2,4-D, as well as those of the commercial herbicide U46D<sup>®</sup> before and after electrolysis (100 mg L<sup>-1</sup> 2,4-D)

### 3.5.2. Biological treatment of non-pretreated U46D<sup>®</sup>

Activated sludge cultures were carried out for two U46D<sup>®</sup> concentrations, 100 and 500 mg L<sup>-1</sup> (Fig. 3). A higher mineralization was observed in the beginning of the culture for 500 mg L<sup>-1</sup> 2,4-D, 33.7% mineralization after 6 days. A rapid DOC decrease was then observed until 8 days culture for both concentrations, until an almost total removal for 100 mg L<sup>-1</sup> initial 2,4-D and 80% degradation for 500 mg L<sup>-1</sup> 2,4-D (Fig. 3a). DOC values then remained nearly constants until cessation of culture, showing that total mineralization could not be achieved for 500 mg L<sup>-1</sup> 2,4-D.

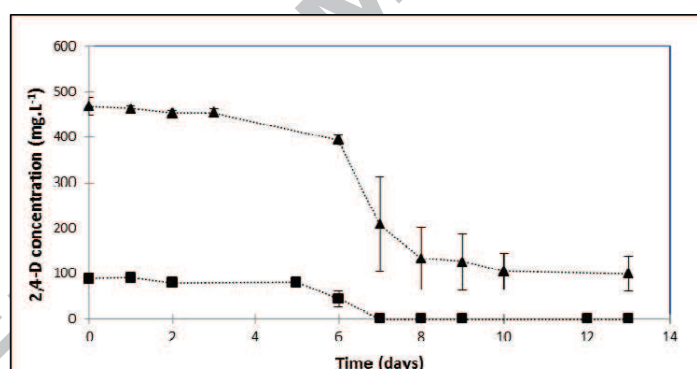
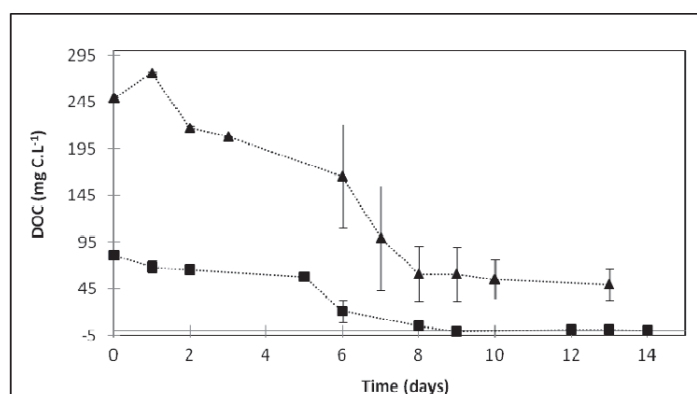


Fig. 3. Time-courses of Dissolved Organic Carbon (a) and 2,4-D concentrations (b) during biological treatment of U46D® corresponding to 500 (▲) and 100 (■) mg L<sup>-1</sup> 2,4-D.

The behavior observed for mineralization was confirmed from 2,4-D monitoring, showing a low target compound degradation until 5-6 days culture (Fig. 3b), which may be considered as an acclimation period; a high degradation rate was then observed until 8 days culture before an almost constant values until the end of culture. Final yields of 2,4-D degradation appeared

to be similar to those of mineralization, with an almost total removal for 100 mg L<sup>-1</sup> initial 2,4-D and 79% degradation for 500 mg L<sup>-1</sup> 2,4-D (Fig. 3b). It should be observed that biosorption, which is a rapid phenomenon, was most likely not involved in target compound removal owing to the low decrease observed during the first day of treatment, in agreement with previous results [52].

If compared to those obtained during biological treatment of pure 2,4-D solutions, these results were confirmed owing to the similar behavior observed [52]. The higher rates observed on the commercial solution are in agreement with the higher BOD<sub>5</sub>/COD ratios described above (0.04 and 0.21 for pure 2,4-D and U46D<sup>®</sup>). These results are most likely related to the presence of dimethylamine salt in the commercial formulation that could increase its “general biodegradability”.

### 3.5.3. Biological treatment of pretreated U46D<sup>®</sup>

Biological treatment was performed on the commercial U46D<sup>®</sup> solution (100 mg L<sup>-1</sup> 2,4-D) pretreated at 200 mA, at flow rates of 1 and 3 mL min<sup>-1</sup> (Fig.4).

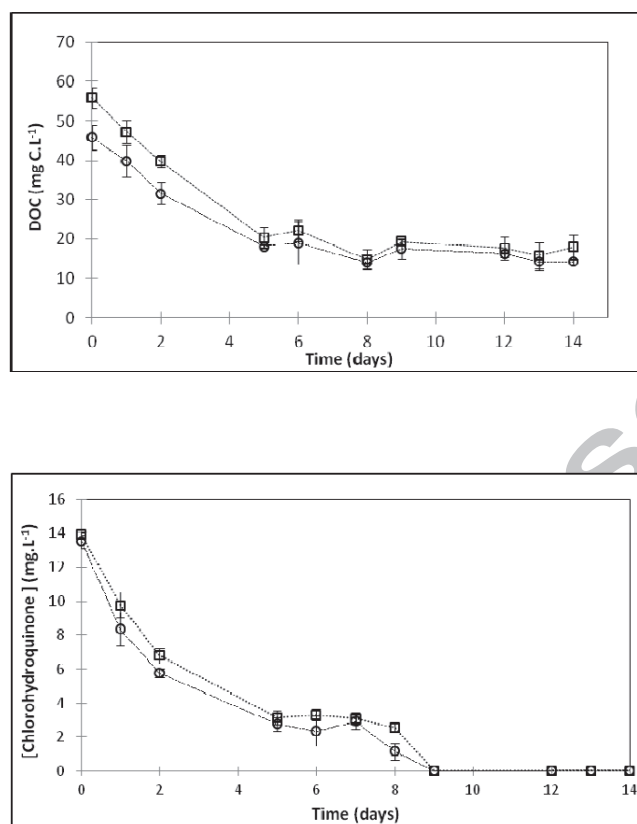


Fig.4. Time-courses of Dissolved Organic Carbon (a) and chlorohydroquinone (b) during biological treatment of U46D<sup>®</sup> corresponding to 100 mg L<sup>-1</sup> 2,4-D, pretreated at 200 mA at a flow rate of 1 (○) and 3 (□) mL min<sup>-1</sup>.

As observed, similar behavior was observed for the two considered flow rates (Fig. 4a): after one day activated sludge culture, 13.1 and 15.6% DOC decrease were obtained for 1 and 3 mL min<sup>-1</sup> flow rates, respectively. This decrease can be attributed to both biosorption and biodegradation phenomena. However, negligible biosorption of the main by-product, chlorohydroquinone, was previously demonstrated [52], showing that biodegradation was mainly involved in DOC decrease. After 5 days culture, 60.3 and 63.7% DOC decrease were obtained for 1 and 3 mL min<sup>-1</sup> flow rates, respectively (Fig. 4a). Low biodegradation rates were then observed until 70.4 and 72.1% DOC decrease obtained for 1 and 3 mL min<sup>-1</sup> after

14 days culture (Fig. 4a), leading to overall mineralization yields during the coupled process of 81.3 and 82.1%, respectively.

These results should be compared to those recorded for non-pretreated U46D<sup>®</sup> for which 98.3% mineralization was observed after 15 days culture, highlighting the persistence of refractory by-products in the pretreated solution, which remained even after 14 days activated sludge culture. As expected [52], this refractory organic matter did not correspond to chlorohydroquinone, since for all studied flow rate, its total removal was observed after 9 days of culture (Fig. 4b), showing the presence of other refractory organic compounds accounting for the residual DOC.

If compared to those previously obtained on pure 2,4-D [52], similar trends were observed for the commercial pesticide U46D<sup>®</sup>. Indeed, the electrochemical pretreatment allowed a significant improvement of the mineralization kinetics and by-products degradation rates; however as also previously shown for 2,4-D, the persistence of low concentrated refractory by-products generated during the electrochemical pretreatment was noticed.

#### 4. Conclusion

A combined process coupling an electrochemical pretreatment and a biological treatment was applied to a commercial herbicide solution, U46D<sup>®</sup>, containing 2,4-D as an active molecule. The electrochemical behavior of U46D<sup>®</sup> was studied by cyclic voltammetry and a similar signal to that of the active molecule 2,4-D was recorded in oxidation around 1.6 V/SCE, confirming that 2,4-D is the major compound in the commercial herbicide. The absence of hydroxyl radicals formation during 2,4-D electrolysis was confirmed suggesting that 2,4-D reacted directly at the electrode surface. Consequently, the proposed pretreatment can be



considered as a 'direct' electrochemical process instead of an advanced electrochemical oxidation process. The impact of the flow rate on the pretreatment efficiency was examined in potentiostatic mode and then in amperometric mode to avoid the need for a reference electrode and hence to be more realistic in view of a future industrial implementation. A flow rate of  $3 \text{ mL min}^{-1}$  appeared to be a good compromise between the pretreatment time (energy cost) and electrolysis efficiency, since it led to an almost total pollutant degradation while mineralization remained limited. Contrarily to pure 2,4-D for which the  $\text{BOD}_5/\text{COD}$  ratio increased, electrolysis did not improve the biodegradability of the commercial herbicide solution. However and even if the limit of biodegradability was not reached (0.4), a biological treatment of the commercial U46D<sup>®</sup> solution was carried out owing to the significant  $\text{BOD}_5/\text{COD}$  ratio measured (0.21).

Activated sludge cultures were then performed on the commercial pesticide U46D<sup>®</sup> electrochemically pretreated or not. The electrochemical pretreatment allowed a significant improvement of the mineralization kinetics and by-products degradation rates; however the persistence of refractory by-products from the electrochemical pretreatment in small quantities was highlighted. To remedy the presence of recalcitrant compounds at the end of the electrochemical pretreatment and to degrade these by-products, possible solutions could be the recycling of the solution in the flow cell on the one hand and an acclimation step of the activated sludge to the electrolyzed solution on the other hand.

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727 Highlights :

728 •Electrochemical/biodegradation combination was tested for pesticide removal.

729 •Total commercial pesticide U46D<sup>®</sup> degradation and 81.2% mineralization were  
730 reached.

731 •A 'direct' electrochemical process was confirmed by the absence of •OH formation.

732 •Biodegradability of the pesticide solution was improved, flow rate was optimized.

733 •The energy cost was found to be similar to those of Advanced Oxidation processes.